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THE MEASUREMENT AND INTERPRETATION OF pH AND CONDUCTANCE
VALUES OF AQUEOUS SOLUTIONS OF URANYL SALTS

by

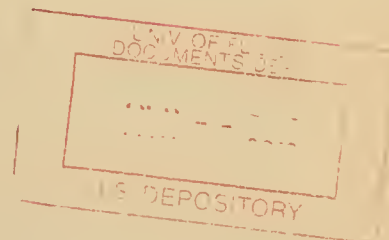
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THE MEASUREMENT AND INTERPRETATION OF pH AND CONDUCTANCE VALUES OF AQUEOUS SOLUTIONS OF URANYL SALTS

By D. A. MacInnes and L. G. Longworth

The hydrolysis of aqueous solutions of the uranyl salts has introduced difficulties in manipulation and in the interpretation of many of the experimental results pertaining to such solutions. It is our purpose to report pH measurements on solutions of UO_2Cl_2 , $\text{UO}_2(\text{NO}_3)_2$, UO_2SO_4 , and $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ together with pH, conductance, and solubility measurements of selected solutions of UO_3 in aqueous HCl . With the aid of these data it has been possible to draw certain conclusions, which are included in this report, regarding the nature of the cations in these solutions and the strength of UO_3 as a base.

Since the corrosiveness of aqueous uranyl salt solutions is due largely to the free acid resulting from hydrolysis, the data reported here should be of value in the prediction and control of that corrosion. Moreover, we have found that the pH and conductance of a given uranyl salt solution may be utilized for the rapid analysis of such solutions on a semimicro scale.

EXPERIMENTAL

Standard solutions of stoichiometric uranyl salts were prepared by solution of a weighed sample of $\text{UO}_3 \cdot (\text{H}_2\text{O})_x$ (previously assayed for uranium by ignition to U_3O_8) in the proper volume of a concentrated standard acid solution, followed by dilution to the desired final volume.

The samples of $\text{UO}_3 \cdot (\text{H}_2\text{O})_x$ used in this work were prepared by two different methods. One sample was obtained by ignition of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, first at 290°C and then at 390°C , until nitric oxide fumes were no longer evolved, after which the cake was pulverized and repeatedly extracted with water. The oxide was then dried in the oven at 150°C , thoroughly ground, again washed with water, dried and heated at 390°C for six hours, and then stored in shallow dishes over a saturated solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The material soon attained a weight sufficiently constant to permit direct weighing and was then assayed for uranium.

The insolubility of uranium peroxide has also been used in the preparation of the oxide. The following procedure has proved practical. One liter of a 10 per cent solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was heated from 60 to 80°C and to this was added slowly, and with continuous stirring, 250 ml of 3 per cent aqueous H_2O_2 . The precipitate was allowed to settle and was then collected on a Buchner funnel. The filtrate had a pH of 0.63 and contained 10 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, thus indicating 90 per cent precipitation of the peroxide. The filter cake was removed, dispersed in 500 ml H_2O and refiltered. This was repeated four times and the successive filtrates had the following pH values: 1.52, 2.45, 3.39, and 4.38. The peroxide was then dried, pulverized, and converted to the oxide by ignition in shallow dishes at 280° for three hours. The product thus obtained was hydrated by suspension in water, followed by drying overnight in an oven at 110°C . The resulting hydrate was again ground and proved to be sufficiently stable in air for direct weighing.

The pH measurements were made at a room temperature of 20 to 25°C with the aid of a glass electrode. The latter was calibrated with 0.05M potassium acid phthalate as pH 4.00.

Table 1. pH values of solutions of stoichiometric uranyl salts.

Concentration equivs/liter	pH				γ^*
	UO_2Cl_2	$\text{UO}_2(\text{NO}_3)_2$	UO_2SO_4	$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$	
0.001	4.05	4.05	4.17	4.76	.99†
.002	3.85	3.85	3.99	4.69	.98†
.005	3.60	3.59	3.76	4.61	.97†
.01	3.41	3.41	3.59 ₅	4.55	.96
.02	3.22	3.22	3.40	4.48	.94
.05	2.95	2.96	3.14	4.36	.92
.1	2.76	2.78	2.91 ₅	4.24	.89
.2	2.58	2.58 ₅	2.67	4.07	.87
.5	2.25	2.25	2.30 ₅		.97
1.0	1.92	1.91	1.97		1.16

† Interpolated

RESULTS

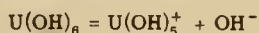
The pH values of stoichiometric solutions of UO_2Cl_2 , $\text{UO}_2(\text{NO}_3)_2$, UO_2SO_4 , and $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ are recorded in Table 1. Since the values for the chloride and nitrate are essentially identical at a given concentration, either set of data may be taken as typical of the behavior of UO_3 with a completely ionized acid. The data for the sulfate, and to a much greater extent for the acetate, indicate the behavior of UO_3 with incompletely dissociated acids.

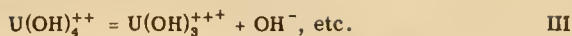
The significance of the values for γ^* in Table 1, and also in Table 2, will be considered later in this report.

The pH and conductance values of mixtures of aqueous HCl and UO_3 at constant ion concentrations of 0.1, 0.5, and 1.0N, respectively, are recorded in Table 2. At a given chloride ion concentration, say 0.1N, the solutions for which the ratio of moles of base to acid i.e., $[\text{UO}_3] / [\text{HCl}]$, is less than 0.5. These were prepared by mixing aliquots of 0.1N UO_2Cl_2 and 0.1N HCl . For values of $[\text{UO}_3] / [\text{HCl}] > 0.5$ weighed increments of UO_3 were dissolved in aliquots of 0.1N UO_2Cl_2 . The change in normality resulting from this latter procedure is quite small and has been neglected in the computations of Table 1.

THE IONIZATION OF UO_3

Uranium trioxide, written with the formula $\text{U}(\text{OH})_6$, is potentially a hexavalent base; therefore, it is of interest to ascertain the nature of the ions that can exist in aqueous solution. Some evidence as to the nature of these ions is furnished by the data of this report. The pH values for the 0.1N solutions of Table 2 are plotted as circles in Figure 1 and show a single point of inflection when the molecular ratio of base to acid is 1/2, that is, $[\text{UO}_3] / [\text{HCl}] = 0.5$. The simplest ionization mechanism that can be assumed is these equilibria





As will be shown, both the pH and conductance data of Table 2 indicate that no appreciable concentrations of U(OH)_3^{+++} exist in aqueous solution. Consequently, the constant, K_3 , for the third equilibrium must be essentially zero and we are left with the problem as to whether or not the uranyl ion, U(OH)_4^{++} (that is, UO_2^{++}), is formed as indicated.

At all pH values at which UO_3 is soluble, the hydroxyl ion concentration is negligible in comparison with that of the other ion species. It is more convenient to write the equilibriums I and II as the equivalent hydrolytic reactions

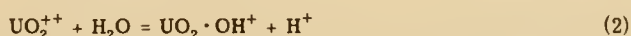


Table 2. Electrometric and conductometric titration of UO_3 .

[UO_3] / [HCl]	[Cl^-] = 1.0		[Cl^-] = 0.5		[Cl^-] = 0.1		γ^*
	pH	κ_{25°	pH	κ_{25°	pH	κ_{25°	
0.000	0.25	0.3326	0.50	0.1786	1.08	0.03899	0.83
.125	.30	.2550	.57	.1387	1.19	.03107	.84
.250	.40	.1818	.64	.1012	1.36	.02341	.85
.375	.58	.1145	.91	.06672	1.64	.01606	.87
.425	.75	.0897	1.11	.05214	1.85	.01319	.88
.450	.89	.0777	1.27	.04647	2.02	.01199	.88
.475	1.14	.0665	1.54	.04019	2.26	.01052	.88
.500	1.92	.0565	2.25	.03499	2.76	.009391	.89
.525	2.45	.0548 ₅	2.64	.03411	3.11	.009104	.89†
.550	2.61	.0542	2.81	.03378	3.26	.009011	.89†
.575					3.34	.008947	.89†
.600	2.73	.0530	2.97	.03321	3.43	.008895	.89†
.625					3.49	.008852	.89†
.650	2.86	.0517	3.08	.03256	3.54	.008822	.89†
.700	2.94	.0503	3.19	.03198			
.750	3.00	.0490	3.27	.03136			
.800	3.06	.0476	3.33	.03071			
.850	3.12	.0461 ₅	3.37	.02999			
.900	3.17				3.80		

† Assumed

As a matter of fact, these equilibria can be made to represent the titration data satisfactorily. The dash curve of Figure 1 was computed with $K_1 = 4.6 \times 10^{-4}$ and $K_2 = 6.0 \times 10^{-5}$. Below the equivalence point, it is identical with the solid curve.

The theory on which these computations are based is this. If we let $x = [\text{UO}_2^{++}]$, $y = [\text{UO}_2\text{OH}^+]$, $z = [\text{UO}_3]$, $h = [\text{H}^+]$, and $a = [\text{Cl}^-]$, in which the brackets indicate gram ion or gram mole concentration, then $K_1y = hz$ and $K_2x = hy$. Electrical neutrality gives the relation, $2x + y + h = a$, and the total concentration of base, b , is $x + y + z = b$. Elimination of x , y , and z between these four relations gives

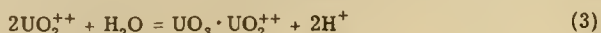
$$b = \frac{aK_1K_2 + (aK_2 - K_1K_2)h + (a - K_2)h^2 - h^3}{2h^2 + hK_2}$$

an expression explicit in b , and hence, suitable for computation.

The simple mechanism represented by the reactions in equations 1 and 2 does not, however, explain satisfactorily the hydrolysis data of stoichiometric uranyl chloride of Table 1. This is shown in Figure 2, in which the pH is plotted against the logarithm of the salt concentration. In this plot, the experimental values are indicated by the circles, while the broken line represents values computed with the aid of the theory and constants suggested. Although these constants are apparent constants and strictly valid only at a concentration of 0.1N, the discrepancy between the observed and computed pH values shown in Figure 2 is probably too great to be attributed to a variation of K_1 and K_2 with ionic strength.

Moreover, the simple theory outlined leads to improbable values for the concentrations of the various ion species in solutions for which $[\text{UO}_3] / [\text{HCl}]$ is greater than 0.5. Thus for $[\text{UO}_3] / [\text{HCl}] = 0.75$, $[\text{UO}_2^{++}] = 0.04454$, $[\text{UO}_2 \cdot \text{OH}^+] = 0.01067$ and $[\text{UO}_3 \text{ undissociated}] = 0.01967$. It is difficult to reconcile the value of 0.01967 for the concentration of dissolved, undissociated UO_3 with the very low solubility of this material in pure water.

The hydrolysis reaction that accounts best for the great majority of our results is



The full curves of Figures 1 and 2 were computed with the constant, K' , for the reaction equal to 1.35×10^{-6} . The theory is this. Letting $w = [\text{UO}_3 \cdot \text{UO}_2^{++}]$, then, $K' x^2 = h^2w$, $2x + 2w + h = a$ (electrical neutrality) and $x + 2w = b$ (total base). Elimination of x and w between these relations leads to the quadratic in b , $2(a - b - h)^2 K' = (2b - a + h)h^2$. For the special case that $a = 2b$, i.e., stoichiometric uranyl chloride, this reduces to $2(b - h)^2 K' = h^3$. Since h is small in comparison with b , $2b^2 K' = h^3$ and $2 \log b + \log 2K' = 3 \log h$; $-\log h = \text{pH} = -2/3 \log b - 1/3 \log 2K'$. Hence, if the pH values of the stoichiometric UO_2Cl_2 solutions are plotted against the logarithm of the concentration, as in Figure 2, a straight line of slope $-2/3$ should result. As explained, this is approximately the case.

As may be seen in Figure 2, the observed pH values of stoichiometric uranyl chloride agree satisfactorily with the computed values for all concentrations below 1N. In Figure 1, the observed and computed pH values are in agreement for all values of $[\text{UO}_3] / [\text{HCl}]$ less than 0.65. Above this, the computed values increase much more rapidly than the observed pH values.

The equation 3 does not, of course, provide for a further reaction of the $\text{UO}_3 \cdot \text{UO}_2^{++}$ ion with water, and hence, cannot account for the relatively low pH of solutions of basic uranyl chloride shown by the difference between the solid and broken lines of Figure 1. Moreover, the reaction $\text{UO}_3 \cdot \text{UO}_2^{++} + \text{H}_2\text{O} = 2\text{UO}_3 + 2\text{H}^+$ is improbable since this leads to appreciable concentrations of dissolved, undissociated UO_3 in solutions for which $[\text{UO}_3] / [\text{HCl}] \geq 1$. This step does not introduce this difficulty $\text{UO}_2^{++} + \text{UO}_3 \cdot \text{UO}_2^{++} + \text{H}_2\text{O} = (\text{UO}_3)_2 \cdot \text{UO}_2^{++} + 2\text{H}^+$. The $(\text{UO}_3)_2 \cdot \text{UO}_2^{++}$ complex will be recognized as the ion obtained by the addition of two protons to uranosic oxide, U_3O_8 , and corresponds to the primary

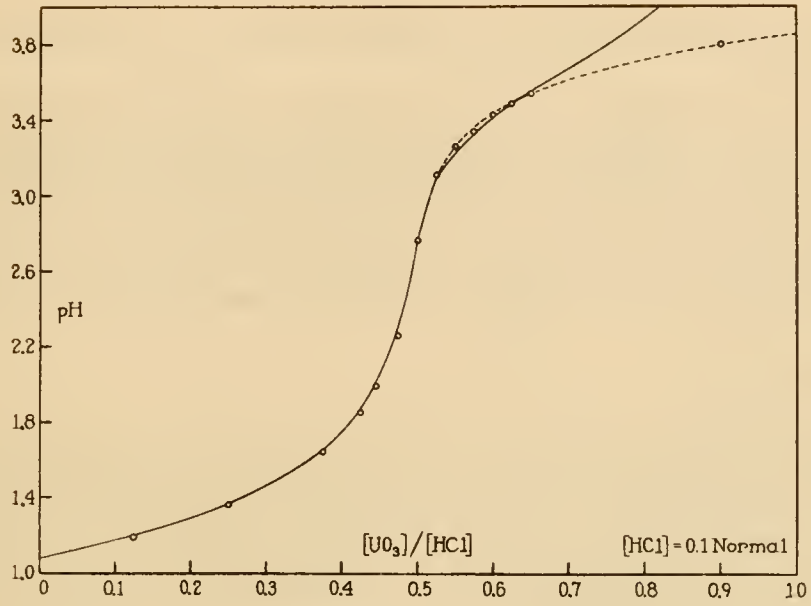
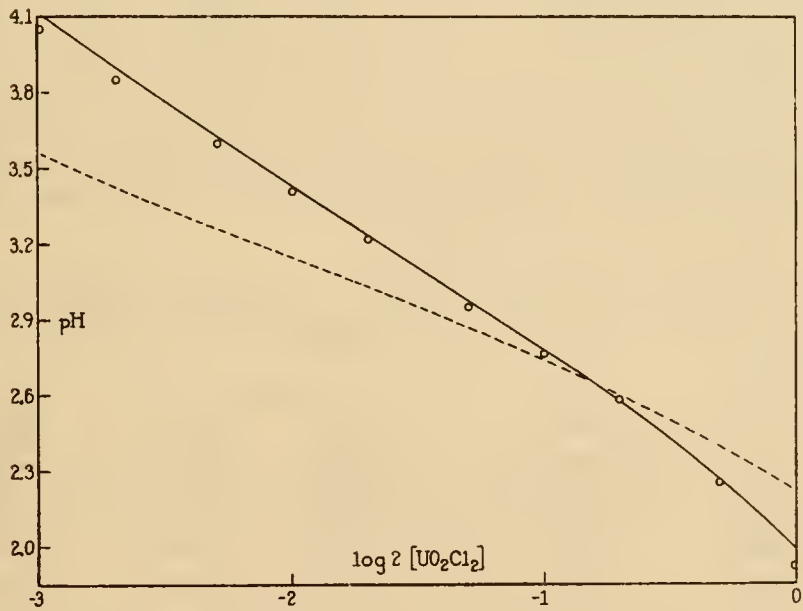


Figure 1.



dissociation of uranium oxide trimer $(\text{UO}_3)_3 + 2\text{H}^+ = (\text{UO}_3)_2 \cdot \text{UO}_2^{++} + \text{H}_2\text{O}$. Cryoscopic measurements on solutions of basic uranyl chloride should tell whether the principle ion in these solutions is $\text{UO}_2 \cdot \text{OH}^+$ or $\text{UO}_3 \cdot \text{UO}_2^{++}$.

In the preceding computations of the various hydrolysis and titration curves, it has been necessary to determine values of the hydrogen ion concentration, $[\text{H}^+]$, from the pH measurements, $\text{pH} = -\log [\text{H}^+] \gamma^*$, in which γ^* is a coefficient that includes both ion interaction effects and a small but unknown liquid junction potential. The values of γ^* used in the computations are recorded in Tables 1 and 2 and were obtained as follows. Taking $\text{pH} = -\log [\text{H}^+]$ as a first approximation, values of $[\text{H}^+]$ were computed for the various solutions of UO_3 . These solutions were then duplicated with the unhydrolyzed Ba^{++} ion substituting for the UO_2^{++} ion and their pH values determined and denoted pH^* . Since the hydrogen ion concentrations, $[\text{H}^+]$, of these mixtures of HCl and BaCl_2 are known accurately $\gamma^* = \text{antilog} (-\text{pH}^*) / [\text{H}^+]$.

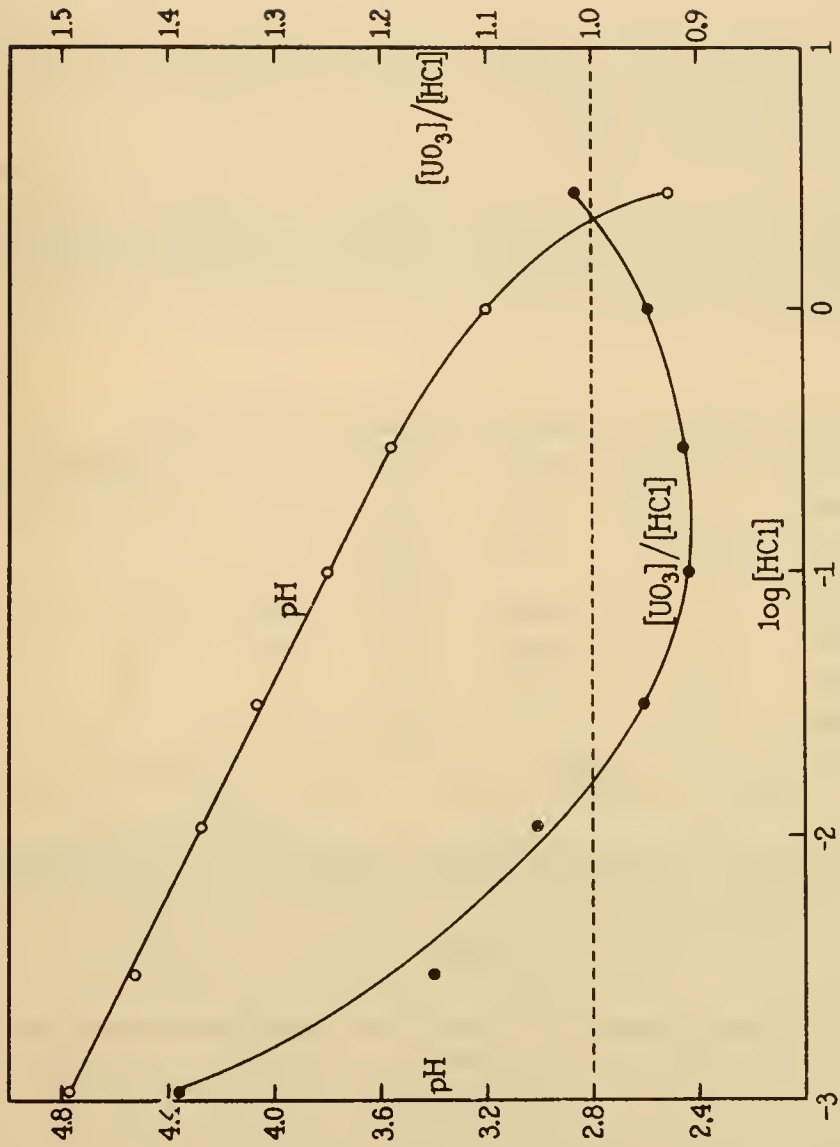
THE SOLUBILITY OF UO_3

We have determined the pH and composition of a great many solutions of aqueous HCl that have been shaken for several days with excess solid UO_3 . The results for a typical sample of oxide are reported in Table 3 and plotted in Figure 3. These data probably do not indicate precisely the solubility of the oxide, however, since the attainment of equilibrium appears to be very slow and different preparations behave somewhat differently. In no case has our saturating phase been homogeneous, nor did it contain an integral number of moles of water of hydration. The water content of the hydrated oxide that is the stable phase at room temperature has not been definitely established, but our results thus far indicate that it is the monohydrate.

Experiments with solutions supersaturated with respect to UO_3 indicate, however, that the solubilities given in Table 3 are low by not more than a few per cent. The basic chloride, $[\text{UO}_3] / [\text{HCl}] = 1$, is a crystalline solid that dissolves, without decomposition, in either a small or a large volume of water. At intermediate concentrations, however, the solution of the basic chloride is accompanied by a slow precipitation of the oxide and the concentration interval over which this hydrolytic decomposition occurs agrees with that portion of the curve in Figure 3, from 0.016N to 2N, in which $[\text{UO}_3] / [\text{HCl}]$ is less than unity. Supersaturation with respect to the oxide may also be achieved by dilution, with water, of a fairly strong solution of HCl saturated with the oxide, and by the addition of NaOH to a solution of the normal chloride. On standing, such solutions usually deposit UO_3 ; analysis of the supernatant has generally given results a few per cent above those of Table 3. In no instance do we have any evidence that UO_3 was dispersed in a colloidal state.

Table 3. pH values and densities of solutions of HCl saturated (approximate) with UO_3 .

$[\text{HCl}]$ moles/liter	$[\text{UO}_3]$	$[\text{UO}_3] / [\text{HCl}]$	pH	d_4^{25}
2.785	2.832	1.016 ₉	2.51	1.7754
1.013	.958	.946	3.20	1.2640
.2979	.2718	.912 ₄	3.56	1.0733
.09909	.0900	.908	3.80	1.0222
.03140	.02986	.951	4.07	1.0056
.01082	.01138	1.052	4.28	1.0004
.00298	.00343	1.15	4.53	-
.00108	.00150	1.39	4.77 ₅	-



EVIDENCE FROM CONDUCTANCE AND TRANSFERENCE DATA
CONCERNING THE IONIZATION OF UO_3

The assumption was tacitly made in computing the curves of Figure 1 that no further dissociation of the uranyl ion to form a trivalent ion of the type $\text{U}(\text{OH})_3^{+++}$ occurred. The close agreement between the observed and computed values of pH for values of $[\text{UO}_3] / [\text{HCl}]$ between 0 and 0.5 justifies this assumption. The conductance data are, however, somewhat more convincing on this point than the pH measurements since the latter are not sufficiently sensitive in the strongly acid solutions in which $\text{U}(\text{OH})_3^{+++}$ ions might be expected to exist.

The observed conductances of mixtures of HCl and UO_2Cl_2 are recorded in the fourth column of Table 4. Values computed with the aid of the assumption that the ion conductances in these mixtures are additive. These are given in the third column. The differences, column 5, are small but slightly greater than the values, column 6, that have been observed for similar mixtures of HCl and CaCl_2 . These differences are explained qualitatively by the Onsager and Fuoss theory as due to the braking action of the slow UO_2^{++} ion on the fast H^+ ion and leave no room for the rather large effects to be expected in the replacement of H^+ ion by $\text{U}(\text{OH})_3^{+++}$.

Table 4. Additivity of ion conductances in mixtures of HCl and UO_2Cl_2 .

1 C_{HCl}	2 $C_{\text{UO}_2\text{Cl}_2}$	3 $\Lambda_{\text{comp.}}$	4 $\Lambda_{\text{obsd.}}$	5 Δ	6 $\Delta(\text{HCl}-\text{CaCl}_2)$
0.1	0.000		389.9		
.075	.025	314.6	310.7	3.9	2.8
.050	.050	239.3	234.1	5.2	4.2
.025	.075	164.0	160.6	3.4	3.3
.000	.100		88.7*		

* Corrected for hydrolysis.

Since the acid present in the mixtures listed in Table 4 suppresses the hydrolysis of UO_2Cl_2 , it was necessary to use as the conductance of that material a value corrected. The equivalent conductance, Λ , of UO_2Cl_2 may be written

$$\Lambda = \lambda_a + \frac{h}{a} \lambda_h + \frac{2x}{a} \lambda_x + \frac{y}{a} \lambda_y \quad (4)$$

if the hydrolysis corresponds to reaction (2). Here x, y, h, and a represent, as before, gram ion concentrations of UO_2^{++} , UO_2OH^+ , and Cl^- ions respectively. The equivalent ion conductances, λ , are proportional to the mobility of the corresponding ion. The mobility of $\text{UO}_2 \cdot \text{OH}^+$, or $\text{UO}_3 \cdot \text{UO}_2^{++}$, is shown later in this report to be 18.5. We may also safely assume, as will be shown, that λ_h and λ_a have the values, 60.86 and 305.2, respectively, as in the corresponding mixtures of CaCl_2 and HCl. From the pH and γ^* values for 0.1N UO_2Cl_2 given in Table 1, $[\text{H}^+] = 0.00195$. Hence, $\lambda_{\text{UO}_2^{++}} = 27.82$ and the equivalent conductance of 0.1N UO_2Cl_2 , after correction for hydrolysis, is 88.68. If the $\text{UO}_3 \cdot \text{UO}_2^{++}$ ion is the hydrolysis product, the last term of equation 4 should be replaced by $2w/a \lambda_w$. However, since the equivalent weight of uranium is the same in the $\text{UO}_2 \cdot \text{OH}^+$ ion as in $\text{UO}_3 \cdot \text{UO}_2^{++}$, neither transference nor conductance measurements can distinguish between the two.

The foregoing ion conductances for 0.1N UO_2Cl_2 correspond to the following transference numbers: $T_{\text{UO}_3} = 0.289$, $T_{\text{Cl}^-} = 0.648$, and $T_{\text{H}^+} = 0.063$. The first two figures are in agreement with values determined experimentally by Kraus and his associates. These values are given in the second line of Table 5, which also includes all of the transference data given in their report for July, 1942.

From the data of Table 2, the equivalent conductances of the solutions listed in Table 5 have been interpolated and are given in the fourth column of that table. The chloride ion conductances, λ_{Cl^-} = $T_{\text{Cl}^-} \Lambda$, are given in column 5. The constancy of λ_{Cl^-} with increasing values of $[\text{UO}_3] / [\text{HCl}]$ above 0.5 affords convincing evidence that the chloride ion is not involved in any of the complexes in these solutions.

The values of T_{UO_3} given in Table 5 are based on an equivalent weight for uranium equal to half of its atomic weight, and hence, represent twice the number of gram atoms of U that are transferred per Faraday. The actual transference numbers for the uranium ions, $x = [\text{UO}_2^{++}]$ and $y = [\text{UO}_2\text{OH}^+]$, are

$$T_x = \frac{2x \lambda_x}{a \Lambda} \quad (5)$$

$$T_y = \frac{y \lambda_y}{a \Lambda} \quad (6)$$

in which a is again the chloride ion concentration. Since the equivalent weight of U in y is twice its value in x ,

$$T_{\text{UO}_3} = T_x + 2T_y \quad (7)$$

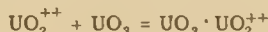
Eliminating $y \lambda_y$ between equations 4, 5, 6, and 7 and solving for x

$$x = \frac{a \Lambda (2 - T_{\text{UO}_3}) - 2a \lambda_a - 2h \lambda_h}{2 \lambda_x}$$

Thus for the solution, Table 5, in which $[\text{UO}_3] / [\text{HCl}] = 0.6565$, $\Lambda = 88.1$, $T_{\text{UO}_3} = 0.372$, and $h = 0.00032$. Therefore, $x = [\text{UO}_2^{++}] = 0.0349$. Moreover, solution of the relations for $y \lambda_y$ and setting $y = 0.06565 - 0.03491 = 0.03074$ gives $\lambda_y = 18.5$.

A 0.1N solution for which $[\text{UO}_3] / [\text{HCl}] = 0.6565$ contains, it will be recalled, 0.01565 moles of dissolved UO_3 per liter of stoichiometric uranyl chloride, per 0.05 gram ions of UO_2^{++} . Hence, if the reaction, on dissolving UO_3 in aqueous UO_2Cl_2 , is simply $\text{UO}_2^{++} + \text{UO}_3 + \text{H}_2\text{O} = 2\text{UO}_2\text{OH}^+$ and goes essentially to completion, that is, no dissolved, undissociated UO_3 is present in solution, the concentration of UO_2^{++} in the solution would be $0.05 - 0.01565 = 0.0344$. The close agreement between this value and that, 0.0349, obtained from a combination of conductance and transference data indicate that the latter are consistent with the ionization mechanism suggested in this report.

If the reaction is



then $[\text{UO}_3 \cdot \text{UO}_2^{++}] = 0.0349/2$ and $\lambda_{\text{UO}_3 \cdot \text{UO}_2^{++}} = \lambda_{\text{UO}_2\text{OH}^+} = 18.5$. As mentioned previously, conductance and transference data cannot distinguish between these two possibilities.

In connection with their transference measurements, Kraus and his associates mention that although $[\text{UO}_3] / [\text{HCl}]$ remained constant in the middle compartment during electrolysis, this ratio always increased in the anode compartment and decreased in the cathode compartment. As the considerations will show, this is consistent with the values of $\lambda_{\text{UO}_2^{++}}$ and $\lambda_{\text{UO}_2\text{OH}^+}$ already derived.

Table 5. Ion conductances of solutions of UO_3 in 0.1N UO_2Cl_2 .

1 [UO_3] / [HCl]	2 T_{UO_3}	3 T_{Cl}	4 Λ	5 $T_{\text{Cl}} \Lambda$
0.490	0.286	0.627	98.2	61.6
.500	.298	.646	93.9	60.7
.503	.298	.654	92.9	60.7
.549 ₅	.297	.679	90.1	61.2
.656 ₅	.372	.692	88.1	61.0
.804	.429	.694		
.977†	.471	.655		

† Precipitation of UO_3 occurred in this solution during electrolysis.

If we consider a cathode compartment of unit volume in which the initial value of $[\text{UO}_3] / [\text{HCl}]$ is b/a and pass 1 Faraday of electricity, $1/2 T_x + T_y$ gram atoms of U will enter this volume, T_a equivalents of Cl^- will leave and 1 equivalent of Cl^- will be formed at the Ag, AgCl cathode. The increase in b , Δb , is $1/2 T_x + T_y$ and that in a , Δa , is $1 - T_a$. The final value of $[\text{UO}_3] / [\text{HCl}]$ is thus, $(b + \Delta b) / (a + \Delta a)$ and this equals b/a only if $\Delta b / \Delta a = b/a$. With the relations $2x + y + h = a$ and $x + y = b$ and equations (5) and (6)

$$\frac{\Delta b}{\Delta a} = \frac{x \lambda_x + y \lambda_y}{2x \lambda_x + y \lambda_y + h \lambda_h}$$

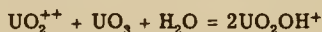
For solutions in which h is small, the term $h \lambda_h$ may be neglected and $\Delta b / \Delta a = b/a = (x + y) / (2x + y)$ only if $\lambda_y = \lambda_x$, which, as we have seen, is not the case. With $\lambda_x > \lambda_y$, $\Delta b / \Delta a < b/a$ and the value of the ratio $[\text{UO}_3] / [\text{HCl}]$ decreases in the cathode compartment as electrolysis proceeds.

SUMMARY

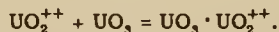
In this document we have reported pH values of aqueous solutions of UO_2Cl_2 , $\text{UO}_2(\text{NO}_3)_2$, $\text{UO}_3(\text{C}_2\text{H}_5\text{O}_2)_2$, and UO_2SO_4 , and pH and conductance measurements on solutions of UO_3 in aqueous HCl . Approximate values for the solubility of UO_3 in aqueous HCl are also included. Although only slightly soluble in water, UO_3 dissolves in aqueous HCl to the extent of about 1 mole of base to 1 mole of acid.

Both electrometric and conductometric titrations of UO_3 with HCl yield, however, a sharp end-point only at 2 moles of acid per mole of base, corresponding to the divalent uranyl ion UO_2^{++} .

The additional solubility of UO_3 in aqueous UO_2Cl_2 may be due to either of these reactions:



or



Conductance and transference measurements cannot distinguish between these two mechanisms. Measurements for pH appear to favor the second process.

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